

A Study of the Mechanism of Graphite Structural Degradation in Lithium-ion Cell Anodes

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Introduction

It has been previously shown that the graphite anodes commonly suffer severe surface structural damage upon prolonged cycling in rechargeable lithium-ion batteries [1,2,3]. This deleterious effect is intensified at high charging rates and elevated temperatures. This is evidenced in the Raman spectra of graphite anodes from tested Li-ion cells by the increased intensity of the carbon D-band ($\sim 1330\text{ cm}^{-1}$) with respect to the G-band (1580 cm^{-1}).

The surface structural disorder that is continuously inflicted in the graphite particles during prolonged charge/discharge cycling modifies the electrocatalytic properties of the graphite, and consequently, affects the thickness and composition of the SEI layer. This effect does not change significantly the electrochemical properties of the graphitic anode. However, the continuous reformation of the SEI layer and reduction of the electrolyte has a significant detrimental effect on the lithium-ion cell long-term behavior. In this study we investigate the mechanism of the surface structural damage in graphite and its effect on the electrochemical performance of the graphite-based anodes. A diagnostic evaluation of these surface-modified model anodes in the Li-ion system is carried out and possible implications for Li-ion cell degradation mechanism are discussed.

Experimental

Thin-film Mag-10 composite anodes (graphite 92%, polyvinylidenedifluoride (PVdF) 8%), were produced. Ar-ion sputtering was used to artificially induce disorder on the surface graphite particles of the electrode. The surface structure and morphology of un-altered and sputtered graphite in composite Mag-10 anodes was analyzed by Raman microscopy and SEM. The SEI layer formed on the electrochemically cycled Mag-10 anodes was examined by FTIR microscopy and GC-MS. All electrochemical measurements were carried out in 1.0 M LiPF₆, EC:DMC 1:1 w/w electrolyte.

Results

The artificially modified Mag-10 anodes showed comparable surface structural disorder to the anodes from cycled Li-ion cells. Interestingly, they displayed twice the amount of irreversible charge capacity during the first formation cycle, compared to fresh un-altered anodes. Impedance spectroscopy and Fourier transform infrared (FTIR) spectroscopy (Figure 1) suggest the formation of a thicker and slightly more resistive SEI layer in the case of surface modified graphite anodes. GC-MS and GPC analysis indicated the presence of compounds with M_w around 1600 g mol^{-1} formed on the surface of modified electrodes. These results may have important consequences for the charge and lithium inventory balance in aged Li-ion cells. Gradual disordering of the graphite anode during prolonged cycling leads to a continuous SEI layer reformation. The charge consumed in this long-term process diminishes the amount of cycleable lithium in the cell and shifts the cathode to a

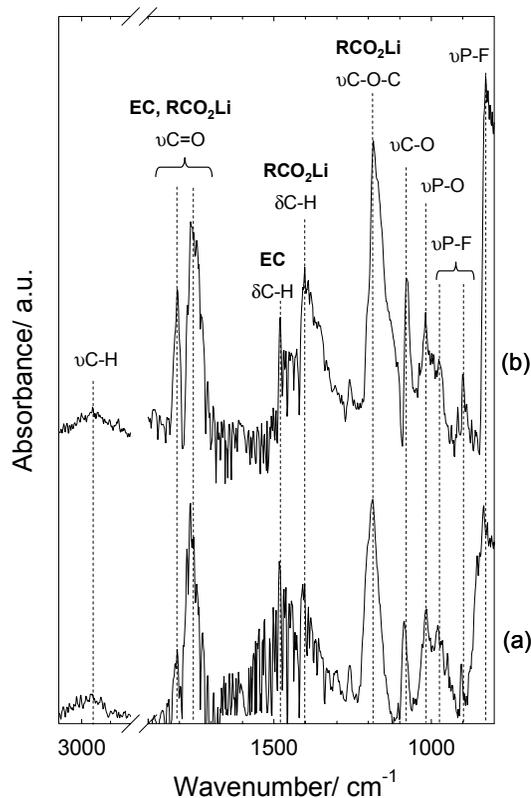


Figure 1. *Ex situ* FTIR microscopy spectra of un-altered (a) and 120s sputtered (b) Mag-10 electrodes after three formation ($C/25$) cycles in 1.0 M LiPF₆, EC:DMC 1:1 w/w.

higher state of charge, reducing the reversible capacity of the cell.

We found that surface disordering on Mag-10 anodes occurs mainly at potentials that correspond to low lithium concentrations in graphite ($1.0\leftrightarrow 0.18\text{ V}$) compared to potentials where stage 1&2 Li_xC compounds are present ($0.15\leftrightarrow 0.005\text{ V}$). Raman mapping of anodes, cycled between these limits for 200 cycles at $C/5$, showed that the I_D/I_G ratio increased from 0.3 for a fresh electrode to 0.45 for deep cycling and 0.6 for shallow cycling. This suggests that the initial phase of lithium intercalation into graphite (ca. $\text{Li}_{0.05}\text{C}_6$) is responsible for most of the damage to the graphite surface structure. The increase of the graphite d-spacing from 3.35 \AA to 3.7 \AA at the edges of graphene domains leads to a local stress build up, and ultimately, the C-C bond(s) breakage across the graphene plane. This effect is likely to be intensified at higher cycling rates or temperatures where faster charge transfer kinetics results in a greater disparity and lithium concentration gradient between the surface and bulk.

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